

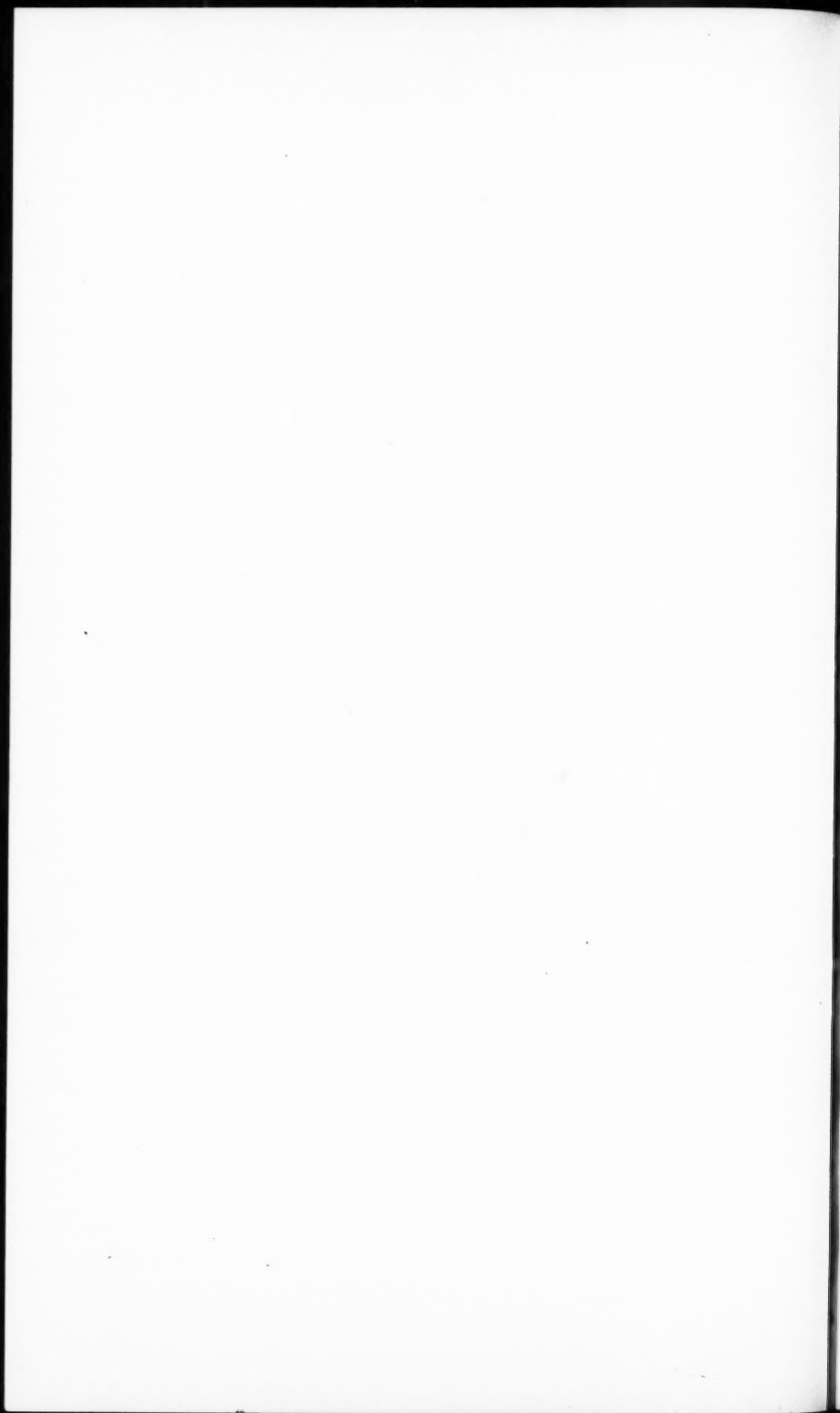
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THE RESISTANCE OF NINETEEN METALS  
TO 30,000 Kg/Cm<sup>2</sup>

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## INTRODUCTION

The pressure range of the following measurements of electrical resistance, 30,000 kg/cm<sup>2</sup>, is considerably greater than that of my previous measurements. My extreme previous range has been 20,000 kg/cm<sup>2</sup>, realized for half a dozen substances only,<sup>1</sup> and almost all my other former work has been restricted to 12,000.<sup>2</sup> My endeavor in this new work has been to pick out those substances for measurement which previous work suggested would be most significant in this new range. Probably the most significant of the new results are those for the minimum resistance of potassium, and the resistances of the new high pressure polymorphic forms of bismuth, caesium, and barium.

## APPARATUS

The extension of pressure range has been made possible by the development of a new type of apparatus. The fundamental principle of this is the same as that of the apparatus for measuring volume changes and polymorphic transitions up to 50,000,<sup>3</sup> namely the application of pressure externally to the pressure chamber to partially compensate for the effect of the internal pressure. The new apparatus is larger and more complicated than the 50,000 apparatus, the volume of the pressure chamber being 16 cm<sup>3</sup> instead of 0.6 cm<sup>3</sup>. The external pressure on the pressure chamber is produced by the independent action of a second hydraulic press, instead of automatically by the action of the same press which produces the internal pressure. Although the second press makes considerable complication, the advantages of being able to vary independently the external and internal pressure more than compensate.

The method by which external pressure is produced on the pressure chamber is the same as in the 50,000 apparatus, namely the pressure chamber is made slightly conical on the external surface, and this cone is forced into a heavy conical sleeve simultaneously with the production of internal pressure. The restrictions set by the cone demand the use of a second press when the size of the apparatus becomes as great as in this apparatus, for if the external pressure were produced automatically by the thrust on the high pressure piston, the angle of the cone would become so small that friction would prevent satisfactory functioning.

The apparatus is shown schematically in Figure 1, which is drawn very approximately to scale, and a photograph of the assembly in Figure 2. A good deal of time was spent in the development of this apparatus, and since there are a number of features which are not entirely straightforward, it will pay to describe the construction in some detail.

Figure 1 shows the double-headed press. The piston of the lower press, with which pressure is produced on the outside of the pressure chamber, is 6 inches in diameter and has a 1.5 inch stroke. The piston of the upper press, which drives the plunger producing the internal pressure, is 3.5 inches in diameter and has a stroke of 4 inches. These two presses are actuated by two hand pumps of my conventional design, capable of exerting a pressure of 15,000 lb/in<sup>2</sup>. Valves and couplings in the lines from pumps to presses enable the pumps to be entirely cut out if necessary, after pressure has been reached, and pressure maintained constant without motion of the pistons. A



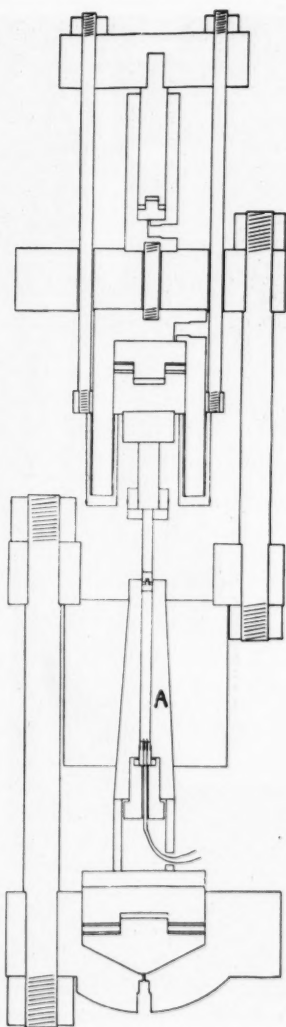


FIGURE 1. Section of the general assembly. The two working presses use three tie rods each, shown in the figures as one. The small cylinder at the top serves to restore the middle piston to its initial position, and plays only a subsidiary part.

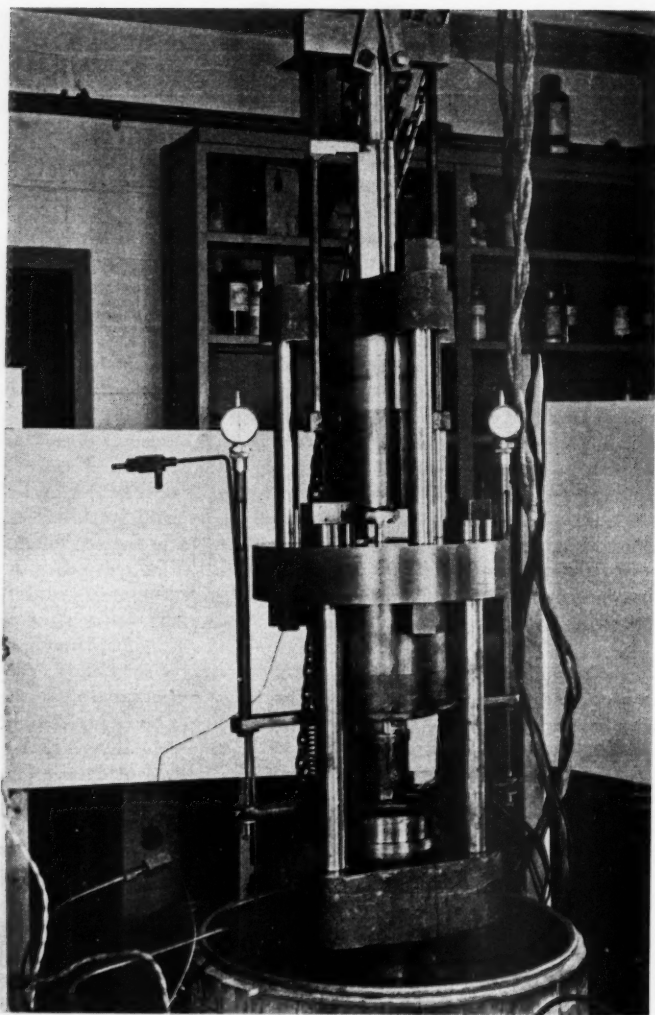


FIGURE 2. Photograph of the complete assembly, ready to lower into the oil bath.

third hand pump is also necessary for operation; this pump produces initial pressure up to  $2,000 \text{ kg/cm}^2$  through a by-pass at the upper end of the pressure chamber by means of an intensifier of my standard design. The only respect in which the priming arrangements differ from the usual ones is in the small size of the connecting tube, which is of nickel, 0.125 inches outside diameter and 0.015 inches inside diameter. This small size was necessary in order to attain the necessary flexibility and ease of handling.

The high pressure chamber, shown at A, is made of "Solar" steel or of "S.M." steel, two somewhat similar steels made by the Carpenter Steel Co. The analyses and heat treatment have been given in previous papers.<sup>4</sup> In addition to great strength and elongation, another advantage of these steels is that they can be enlarged with a reamer without glazing the reamer when in a state of hardness materially greater than that possible with most other steels. In use, there is some wear of the inner surface of the cylinder, so that it is necessary to re-ream the hole from time to time. For this purpose there are four reamers of high speed steel, respectively of 0.490, 0.500, 0.510, and 0.520 inches diameter. All the measurements in the following were made with a single high pressure chamber, starting at 0.490 and ending at 0.520. I am not planning to enlarge the hole further, but shall discard the chamber when the present size, 0.520, becomes too much worn.

The pistons are made of carboloy, for which I am much indebted to the Carboloy Co. of America, and Dr. Zay Jeffries. Because the internal diameter of the pressure chamber may actually decrease when external pressure is applied, it is necessary, in order to avoid pinching the piston into the cylinder, to make the diameter of the carboloy piston less than the diameter of the hole. A clearance of 0.005 inches has proved adequate. Four carboloy pistons are therefore required, respectively 0.485, 0.495, 0.505, and 0.515 inches diameter. In spite of the fact that 30,000 is much less than the crushing strength of carboloy, which I have found to be as high as 65,000, the pistons will not stand up indefinitely, but very soon fine longitudinal cracks appear, which slowly increase in size and number, until eventually the piston fails by splitting into longitudinal prisms. Failure begins at the lower end of the piston, where it is in contact with the moving plug. Failure might also begin at the top end if it were not prevented there by a very heavy hardened steel collar, with a  $0.5^\circ$  taper, forced around the upper end of the piston. Two grades of carboloy piston were tried. The first grade, number 905, has the highest compressive strength of

any of the grades of carboloy, and is the variety used in my work to 50,000. The second grade, number 883, has a lower compressive strength, but a higher strength in tension, that is, it permits a greater elongation without rupture. For this reason it seemed that longitudinal cracks might be less likely to form. As a matter of fact, not much difference could be found between the two grades for present purposes.

In order to permit an approximate evaluation of the distortion of the pistons under pressure, I made a rough determination of Young's modulus and Poisson's ratio. These were respectively, for grades 905 and 883:  $E = 99 \times 10^6$  lb/in<sup>2</sup>,  $\sigma = 0.267$ ; and  $E = 92 \times 10^6$ ,  $\sigma = 0.359$ .  $\sigma$  was measured directly from the lateral expansion under compressive load.  $E$  has been measured before at the Bureau of Standards for carboloy, and these extraordinarily high values checked. Poisson's ratio apparently has not been previously measured. The great difference for the two grades was a surprise. There seemed nothing obviously wrong with either measurement. Perhaps the material is not very homogeneous. In any event, the distortions of the piston up to the extreme pressures reached here, 30,000 kg/cm<sup>2</sup>, are small; the piston shortens by 0.5 per cent, and expands laterally by less than 0.001 inch, well within the clearance limit.

The leak-proof plug pushed by the carboloy piston is of the mushroom "unsupported area" type which I have used in all my work. 30,000 kg/cm<sup>2</sup> is about the limit which such a plug will stand in the best grade of steel that I have been able to find, failure being by pinching off the stem of the mushroom. A plug can seldom be used for more than three or four excursions to 30,000, and in fact many times pinching off has progressed to such an extent after two applications that the plug has been discarded. It was only by special design that it was possible to carry the plug to this pressure at all. The construction is shown in Figure 3. The plug is made of "Seminole Medium" steel of the Ludlum Steel Co., quenched into oil instead of into water, and drawn to a Rockwell C hardness of 59. The stem of the mushroom is made shorter and smaller in diameter than usual, in this way cutting down the excess pressure in the packing. Packing only 0.125 inches thick is used; this makes the stressed part of the stem so short that it receives effective support from the massive head. "Duprene" packing is used instead of soft rubber. The packing itself is prevented from leaking by the conical rings shown in Figure 3. The rings are made of Cr Va steel, either untreated or else hardened and drawn back nearly to the initial softness. Ordinary mild

steel is unsuitable for these rings because it extrudes between mushroom and cylinder walls. The piece *T*, by which the mushroom is pushed by the carboloy piston, is made of "Teton" steel, left glass hard. Surprisingly, no trouble was experienced from the upsetting of this, doubtless because of its shortness and the frictional support of the ends.

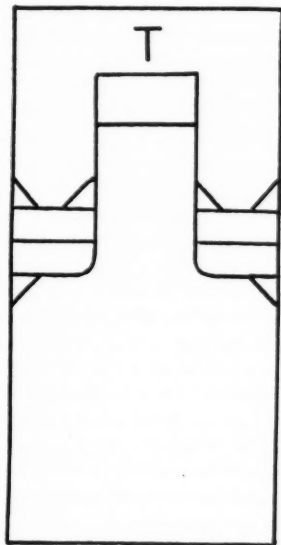


FIGURE 3. Details of the moving plug.

The outside of the pressure vessel *A* (Figure 1) was ground to a taper of 1 inch (on the diameter) per foot of length. The smaller the taper, the larger the external pressure on the external surface attainable with a given thrust. The smaller the taper the better, therefore, except for the limitations imposed by friction. My first experiments with this apparatus were made with a taper of 1.125 inches per foot. Comparative studies of the friction effects with the two tapers led to the conclusion that the smaller taper was superior.

The conical collar supporting the pressure chamber on the outside has to support an internal pressure of close to the maximum allowed

by its tensile strength, so that it is important to get the best construction. A number of these collars were ruptured before success was attained. The total thickness of the collar is 6.375 inches; it was made from three discs, each 2.125 inches thick. The advantage in making it in three discs is that thus each disc is thin enough to receive nearly the maximum benefit from heat treatment throughout its entire mass. The discs were made of "Solar" steel, the central hole forged into the disc, and then the disc hammered around a tup through the central hole, so that there was some working of the fibres circumferentially. This circumferential forging proved essential; without it the discs break. The discs were hardened, drawn to a Rockwell C hardness of 53, ground flat and parallel on both faces, and the central hole ground to the required taper, but a little smaller than final dimensions. Each ring was then stretched separately by forcing into it a solid conical piece of the same taper as the pressure chamber, until a permanent stretch of the order of 5 per cent was produced. With suitable allowance for friction, the maximum pressure reached during the stretching process was about 15,000 kg/cm<sup>2</sup>. The elastic distortion of the ring corresponded to an elastic displacement of the internal cone along its axis of 0.4 inches at the maximum. The three rings having been separately stretched, they were then clamped together, and the hole ground to final dimensions in all three simultaneously. I have had only one failure of a ring in the final apparatus.

Lubrication between the pressure chamber and the collar was by the same method as used in the 50,000 apparatus, namely a paste of graphite, water and glycerine, smeared on both sides of a sheet of 0.002 inch lead interposed between collar and cone. The details have been described in the preceding paper,<sup>5</sup> as also the method of evaluating friction by measuring the axial displacement of the cone as a function of thrust with increasing and decreasing pressure. A quantitative study was made in this way of the frictional effects in this apparatus, and the effective over-all friction found to be of the order of 5 per cent. That is, if the thrust on the 6 inch piston was such as to indicate by a calculation neglecting friction that the external pressure on the pressure chamber was 10,000 kg/cm<sup>2</sup>, the actual external pressure was 9,500.

During the actual measurements, at the top pressure of 30,000, very nearly the maximum pressure of which the apparatus was capable was applied to the 6 inch piston, namely 14,500 lb/in<sup>2</sup>. The effective thrust exerted by the 6 inch piston is diminished by that exerted by the 3.5 inch piston, since the two pistons oppose each other.

At 30,000 kg/cm<sup>2</sup> the pressure on the 3.5 inch piston was about 10,000 lb/in<sup>2</sup>. Since the ratio of the areas of the two pistons is 0.34, the effective pressure exerted by the 6 inch piston is approximately 11,000 lb/in<sup>2</sup>. Making allowance for friction, this means a pressure of approximately 10,000 kg/cm<sup>2</sup> on the outside of the high pressure cone. In the previous paper will be found the material from which the distortions may be calculated. 10,000 external pressure produces on the inside a contraction numerically equal to the expansion produced by an internal pressure of 15,000. This is an approximate measure of the increase of range made possible by the external pressure. As a matter of fact, in practise the external support seemed to be even more effective than this very rough theory would indicate. The same high pressure chamber was used for all the measurements reported in the following, representing nearly 50 applications of 30,000. This is in striking contrast to the half dozen or so applications which was the best that could be obtained with the former unsupported cylinder to only 20,000. Furthermore, the high pressure cylinder did not receive for this work any preliminary stretching, such as has always been necessary before. It was a very great convenience to be able to dispense with the preliminary stretching, which becomes very awkward if the entire bore has to be stretched uniformly.

It appears, therefore, that by the use of external support as in this apparatus, the weakest part is no longer the pressure chamber itself, but failure occurs at other parts of the apparatus. The limit set by the pinching off of the mushroom stem of the moving plug is not far above 30,000, but the limiting feature in the actual experiments was the insulating plug by which the leads were taken in at the lower end for electrical measurements. There are two major causes of failure in any ordinary type of insulating plug: pinching off of the lead itself, and extrusion of the insulating material through the annular space where the lead leaves the pressure chamber. It is ideally possible to overcome both these weaknesses simultaneously and make a plug that will withstand a single application of any pressure, no matter how high, merely by making the column of insulating material long enough. The frictional resistance to extrusion afforded at the walls of a cylinder increases enormously with the length, the stress at the exit end dropping off exponentially with increasing length. Since it is the stress at the exit end which determines the pinching off and extrusion, these two effects can be easily eliminated if the length is great enough. The difficulty comes when one attempts to apply the pressure a second time. On the first release of pressure, expansion of

the insulator forces the stem to pull itself back through the insulator, which may exert such great friction because of its length that the stem pulls itself in two. If a plug is to be used more than once, some sort of compromise has to be effected, by suitably choosing materials and dimensions, between the friction on increasing pressure, which is advantageous, and friction on decreasing pressure, which is fatal. In the first place it is obviously an advantage that the insulating stem should be of the maximum strength. Tungsten wire would seem indicated for this purpose; it was a great disappointment to find that the fibrous structure of ordinary tungsten wire is so pronounced that under the conditions encountered in these plugs the wire disintegrates into longitudinal fibres. It was necessary, therefore, to return to commercial piano wire. In order to stiffen this beyond its commercial condition, I drew it down from 0.0140 inches to 0.0135 inches through a diamond die. This extra step in the drawing resulted in a very appreciable increase of strength. For the insulator, various materials were tried. Sapphires, which had proved effective to 20,000, were completely fractured by a single excursion to 30,000. Solenhofen limestone, which was, perhaps, first suggested at the Geophysical Laboratory in Washington, in proper combination with mica, proved effective. It is necessary to select a suitable piece of limestone with some care; much of the commercial material is too soft. Recently I have been successful with a construction replacing most of the limestone with steel, suggested by Mr. Charles Chase.

The detailed construction of the plug is shown in Figure 4. The steel parts of the plug require care in construction, since 30,000 kg/cm<sup>2</sup> is pretty close to the limit that any steel, even in the glass hard condition, will support in compression indefinitely without some yield. The steel used was "Teton," drawn to give a Rockwell C hardness of 59. The projecting end was ground to an angle of 1°, and reinforced by being forced into a collar of heat treated Cr Va steel, C. This collar prevented spreading and cracking of the projecting end, which otherwise always took place. The plug carries four insulated leads, one for the manganin gauge and three for the measurement of various resistances by the potentiometer method. The apparatus itself is the common ground of the manganin gauge and the fourth of the potentiometer terminals. I was never able to construct a plug which I could count on to use for more than two excursions to 30,000; this was sufficient for measurements on a single substance at 30° and 75° with a single set-up. Even as it was, the two runs were often not complete. Attempts to use the plug for two more runs were sometimes successful,



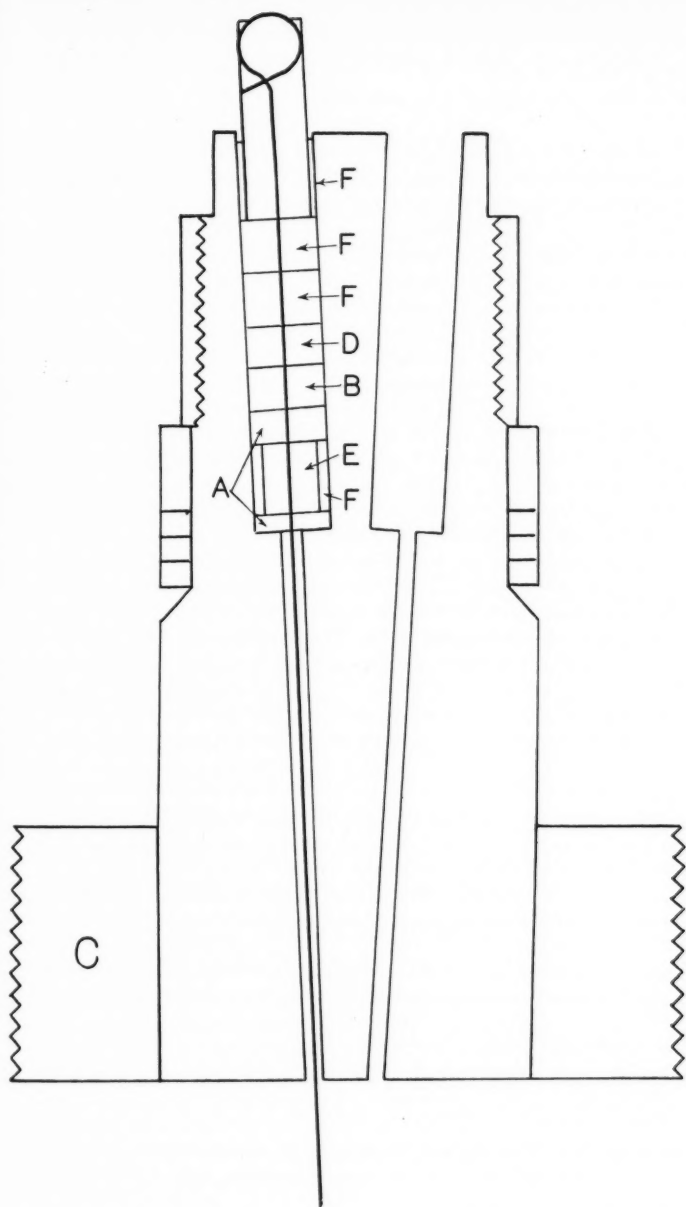


FIGURE 4. Assembly of the insulating plug. A, mica; B, soft rubber; D, Duprene; E, hardened steel; F, pipestone.

but more often than not one of the four terminals went wrong. The chances of success are obviously much less with four terminals; if only a single terminal had been involved it probably would have been economical to continue with the same plug until it failed, but with four it seemed best to reassemble the plug after two runs with a single substance. Such frequent reassembly of the plug was very time consuming, and it was the limitations imposed by the plug that mainly restricted the amount of data that could be turned out in a given time. Because of this limitation of output, I had to try to choose my materials for measurement so as to give the totally most useful information. This is the reason that some of the data in the following are incomplete. If, for example, a successful run had been made at  $30^{\circ}$ , and then at  $75^{\circ}$  the plug failed, making necessary a new set-up in any event, I usually preferred to make the new set-up with a new substance, leaving the data for the first substance incomplete, hoping to come back to it later, perhaps.

As already intimated, resistance measurements were made at two temperatures:  $30^{\circ}$  and  $75^{\circ}$ . Temperature was maintained by putting the entire lower part of the double press, up as far as the carboly piston, in a thermostated oil bath. The entire press, which weighs in the neighborhood of 1,000 lb., was handled by a chain hoist, traveling on an I beam attached to the ceiling. The thermostating arrangement was conventional enough, and does not need description. The heating was electrical. The amplitude of the temperature cycle in the bath was seldom as much as  $0.05^{\circ}$ , and the period was of the order of ten minutes at  $75^{\circ}$ . There was no appreciable drift of temperature during a run. Temperature equilibrium is reached only slowly in masses as large as this, and without some device it would have taken an entire day to reach temperature equilibrium before starting a run. The device was adopted, when raising the temperature, of running the temperature of the bath beyond the final temperature, and then allowing it to drop back. It was thus found possible, after some experimenting, to make the change of temperature from  $30^{\circ}$  to  $75^{\circ}$  in from one and one half to two hours. After each increase of pressure it was necessary, as usual, to wait for the heat of compression to be dissipated, but there was nothing unusual in this situation. At the lower pressures readings could be made in from seven to eight minutes after a 5,000 kg increment of pressure. At the higher pressures the thermal conductivity of the pressure transmitting medium had become so much greater that readings could be gathered as fast as the various instruments could be read, a reading perhaps every three or four minutes.

Pressure was measured in terms of the change of resistance of a coil of manganin wire. The manganin resistance has been directly calibrated<sup>6</sup> only to 13,000 kg/cm<sup>2</sup>; up to this pressure, change of resistance is linear in the pressure within 0.1 per cent. The pressures beyond 13,000 had to be extrapolated. There are, however, various indications as to the general goodness of such an extrapolation. There is in the first place the internal evidence of the resistance measurements themselves. An argument from this point of view has already been used in connection with my measurements to 20,000.<sup>7</sup> If the pressures, as determined from the resistances of several different substances, all extrapolate to the same value, then the presumption is that none of the extrapolations is far wrong. In the following will be found data for the resistances of copper, silver, gold, and iron discussed from this point of view. The point of using just these four metals was that they were conveniently available, and their resistances are more nearly linear than that of many other metals, so that extrapolation is less hazardous. Extrapolation of other phenomena than resistance would also give a basis for an estimate of the true pressures. In the following will be found a measurement of the melting pressure of mercury at a temperature of 75°. The melting curve of mercury has previously been followed up to 20°, where the melting pressure is 11,600 kg/cm<sup>2</sup>. Extrapolation of the previous melting curve to 75° by assuming constant second differences (the first vary only slightly, so that the departure from linearity is only slight) indicates a melting pressure of 22,595 at 75° against 22,570 measured with the manganin gauge. Another sort of estimate can be obtained from the melting curve of ice VI. Formerly I had followed this curve up to 21,000 in terms of the manganin gauge,<sup>8</sup> all pressures above 13,000 thus being extrapolated. I have recently redetermined a point on this curve with the 50,000 apparatus; pressure in this is determined by measuring the actual thrust on the piston, that is, it is essentially an absolute gauge determination. At 80° the new melting pressure does not differ from the previous value by more than 200 kg/cm<sup>2</sup>, indicating an error in the manganin gauge at 20,000 or not more than the difference. Finally, it is possible to make what is essentially an absolute calibration of the manganin gauge to 30,000 in terms of the actual thrust on the piston with which pressure is produced. Of course the objection to this method is the insensitiveness due to friction, but within the limits imposed by friction the results should have absolute significance. It turned out, furthermore, that the frictional effects were surprisingly low. The total friction on the 3.5 and the 6 inch

pistons of the press together was less than 3 per cent, determined by pushing first one piston with the other and then inversely. Furthermore, the friction at the high pressure moving plug was much less than in my other apparatus. This was due to a combination of factors. The "Duprene" packing was not as thick as usual; the external pressure on the cylinder prevented the interior from expanding as much as formerly, so that the extrusion of the soft steel rings, with which the "Duprene" was retained, into the annular space between hardened mushroom and cylinder walls was almost negligibly small (this is usually the major source of friction), and the clearance between cylinder walls and carboloy piston was sufficient to remove all friction at this point. Measurements were made of the resistance of the manganin in terms of the pressure on the pistons of the press, taking the means with increasing and decreasing pressure. In the neighborhood of 25,000 the means with increasing and decreasing pressure differed by something of the order of 10 percent, that is, the piston just started to move in at 7,800 lb/in<sup>2</sup> on the 3.5 inch piston, and just started to move out at 7,000. Making a one per cent correction for increase of cross section of the cylinder at 25,000, the piston pressure was 25,300 against a manganin pressure of 25,000. The agreement is better than I had anticipated. All in all, it seems probable to me that the manganin pressure gauge is not in error by more than 1 or 2 per cent, and there is no certain evidence that it is in error at all.

The manganin gauge was constructed of double silk covered wire 0.003 inches in diameter, obtained from Driver Harris Co., and of American manufacture. The wire was from the same spool as the gauges which I have used in various measurements at liquid air temperature.<sup>9</sup> The total resistance of the gauge was about 65 ohms. It was wound as usual non-inductively into a coreless anchor ring, the dimensions being about 6 mm. overall outside diameter, and 3 mm. thickness. It is thus materially smaller than my other gauges, a feature made necessary by the limitations of space. It is so small that in the pressure apparatus it could be mounted on its side between a couple of the terminals of the insulating plug. Calibration was as usual in terms of a single fixed point, the freezing pressure of mercury at 0°C, taken as 7640 kg/cm<sup>2</sup>. Calibrations were made independently at 30° and 75°; the constant is 0.6 per cent greater at 75° than at 30°. The coil was seasoned by a preliminary heat treatment at atmospheric pressure for eight hours a day for seven days to 140°, and then by a couple of preliminary applications of the full 30,000. Whatever the explanation, the seasoning was unusually effective, and the drift of

zero has been conspicuously less than with some of my other gauges.

During the preliminary work with this apparatus a quantitative study was made of a number of features not yet mentioned. (1) The stretch of the tie rods of both the 3.5 and the 6 inch press was determined with increasing and decreasing pressure. (2) The two pistons were directly coupled together and the pressure determined, over the entire range of pressure, which was required by either to push the other, giving in this way the packing friction. (3) The external expansion of the retaining rings was determined as a function of pressure. (4) Finally, the internal contraction of the pressure chamber was determined when it is pushed into the supporting rings by the 6 inch piston, with no internal pressure. There is no need for the purposes of this paper to describe all these measurements in detail, but they had great value in permitting a complete picture of the functioning of the whole assembly.

The pressure liquid was iso-pentane; this has the lowest freezing point of any readily available liquid not boiling below room temperature. One of the routine measurements always made was to record the position of the piston as a function of pressure; the freezing of the iso-pentane would have been shown by a discontinuity in the motion. No such discontinuity was ever found, nor any other evidence of the freezing of the iso-pentane. The iso-pentane was of ordinary commercial grade, obtained from the Eastman Kodak Co. It may be that it contained sufficient impurity to materially depress the freezing point, or possibly freezing was suppressed altogether, although the freezing range may have been entered, because of viscous resistance to formation of the nuclei of the solid phase. Whatever the reason, the failure to freeze was fortunate, and a pleasant surprise.

The actual routine of the measurements does not need much detailed discussion. Usually readings were made at 5,000 intervals up to 30,000, and then with decreasing pressure at 27,500 and at 5,000 intervals thereafter. Practically never was there any perceptible hysteresis. Since the boiling point at atmospheric pressure of iso-pentane is less than  $30^{\circ}$ , it was not possible to start from dead zero at  $30^{\circ}$ , but a zero was used of a few hundred kilograms. Extrapolation to zero should introduce no appreciable error. At  $75^{\circ}$  the pressure of the lowest reading was usually in the neighborhood of 2,000, so that there is perhaps more possibility of zero extrapolation error, but it should not be important in any event. The zero of the manganin gauge at  $75^{\circ}$  was usually checked by completely removing the moving plug and letting the iso-pentane boil out. Sometimes it was possible

to get also the zero of the resistance under investigation under the same conditions, but the temperature sensitivity is much greater than that of the manganin, and the temperature fluctuations in the isopentane vapor were usually too great to permit this.

In addition to the electrical measurements, as a matter of routine, record was always made of the pressure on the 6 inch and the 3.5 inch pistons, the motion of the pressure chamber into its conical collar, and the motion of the carboloy piston. These data were seldom used,<sup>†</sup> but sometimes they proved convenient. Thus it was possible to check at any time the friction of the cone in the collar; this check was made at intervals during the progress of the work, and no progressive change found. From the motion of the carboloy piston it should also be possible to get an approximate value for the compressibility of isopentane.

The detailed data now follow.

#### DETAILED DATA

*Copper, Silver, Gold.* The material on which these measurements were made consisted of the identical coils of my original measurements in 1916. The wire was double silk covered, wound non-inductively on itself into a coreless toroid, with resistances of 41, 24, and 20 ohms respectively. Because of the high resistance, the technique of measuring the resistance was different from that used for the other metals, all of which had a much lower resistance. Fluctuating resistance at the contacts is not a factor when the resistance is as high as this, so that the resistance of these three metals could be measured on the same Carey Foster bridge that was used for the manganin resistance gauge. A bridge measurement of this sort demands only two leads; since the insulating plug had four leads, all four coils, manganin, copper, silver, and gold, were connected to the plug and measurements made on all four at each pressure. One or the other resistance was connected to the bridge through a simple arrangement of mercury switches. The relative measured decrements of resistance of these three metals are thus independent of any failure of perfect reproducibility in the manganin gauge.

These measurements were the first made with the pressure apparatus, and there were various hitches in getting the apparatus to functioning properly, there being trouble from leak, or short or open circuit of the insulating plug. Two attempts were made at 30° and two at 75° before the final runs, which were carried through successfully with a single set-up. The experimental points lay with great

smoothness, but there was a consistent difference between the increasing and decreasing runs simply described as due to a continual creep of zero toward high values during the application and release of pressure. The effect was much larger at  $75^\circ$  than at  $30^\circ$ , where it was barely perceptible. The maximum zero creep was in copper at  $75^\circ$ , for which it was about 0.5 per cent of the maximum effect of pressure, that is, an increase of the original resistance by 0.00025 of itself during the run. The effect was thus always small, and there is no more reason to be concerned about it than about the seasoning effects which have been found so many times at lower pressures, even if the present effect is somewhat larger than formerly. The mean of results with increasing and decreasing pressure was taken.

The results are given in Table I. These present values may be checked against the results obtained on the same specimens 20 years ago.<sup>10</sup> At  $30^\circ$  and 10,000 kg/cm<sup>2</sup> the former values for  $-\Delta R/R_0$  for copper, silver, and gold were 0.01826, 0.03386, and 0.02942 respectively against 0.01857, 0.03376, and 0.02934 found now. The differences are small, and there is no consistent difference of direction, as there would be if there were important error in the measurement of pressure. I see no reason to think that the effects may not be connected with the pressure seasoning. Notice that at low pressures the pressure coefficient of copper decreases with rising temperature, an abnormal result checking the result previously found, but that between 15,000 and 20,000 the sign reverses, becoming normal.

It is of interest to inquire whether there is any notable new trend in the results at pressures above 12,000, the previous maximum. This question may be answered by extrapolation from the low pressure values. A second degree curve may be passed through the points at 5,000 and 10,000 and the curve extrapolated to 30,000. It will be found that the value of  $-\Delta R/R_0$  given in this way is in all three cases too small, but not by a large amount. The numerical excess of the actual  $\Delta R/R_0$  over that calculated is 5.23, 1.79, and 3.74 per cent respectively for copper, silver, and gold. The difference is in such a direction that the second degree extrapolation would predict a minimum at too low a pressure. Simple linear extrapolation from 10,000 and 0 would fail by two or three times as much.

Obviously only a rough significance can be attached to this result. There is no particular virtue in the second degree curve, and in fact it was already known that the experimental results to 12,000 could not be reproduced to within quite the experimental error by a second degree curve. But roughly, one significance of the fact that extra-

TABLE I

RESISTANCE DECREMENTS OF COPPER, SILVER, GOLD, IRON, LEAD

Pressure kg/cm <sup>2</sup>	Copper		Silver		Gold		Iron		Lead	
	$-\Delta R/R_0$		$-\Delta R/R_0$		$-\Delta R/R_0$		$-\Delta R/R_0$		$-\Delta R/R_0$	
	30°	75°	30°	75°	30°	75°	30°	75°	30°	75°
5,000	.0096	.0094	.0174	.0176	.0151	.0154	.0121	.0118	.0686	.0691
10,000	.0186	.0185	.0338	.0341	.0293	.0299	.0234	.0232	.1266	.1277
15,000	.0271	.0271	.0492	.0497	.0429	.0437	.0341	.0341	.1770	.1791
20,000	.0354	.0354	.0637	.0644	.0559	.0570	.0444	.0447	.2214	.2242
25,000	.0434	.0435	.0774	.0784	.0684	.0698	.0542	.0548	.2611	.2643
30,000	.0513	.0514	.0904	.0916	.0806	.0724	.0637	.0646	.2959	.2998



polarization over a pressure range of three fold does not fail by more than a few per cent is that the manganin gauge pressure is probably not in error by any large amount.

With a relation so nearly linear as that found, it would be profitless to speculate about the existence of a pressure of minimum resistance.

*Iron.* The measurement of iron was undertaken in much the same spirit as that of copper, silver, and gold, namely because the effect of pressure up to 12,000 does not depart much from linearity, so that some presumptive evidence can be obtained as to the accuracy of the manganin gauge. The same sample of iron was used as had been previously measured up to 7,000 in the gas apparatus at liquid air temperature,<sup>11</sup> and also in my work of 1916. A short specimen was used, and the measurements were made with the potentiometer, as were the measurements on all subsequent metals.

After one failure, successful runs were made to 30,000 at 30° and 75° with a single set-up. Again the points lay very smoothly with a slight zero creep in the same direction as before, the maximum creep at 75° being less than 1 per cent of the pressure effect or 0.0005 of the initial resistance.

The results are given in Table I. Second degree extrapolation from 5,000 and 10,000 gives at 30,000 a  $\Delta R/R_0$  too small numerically by 6.5 per cent on the measured value.

*Lead.* The specimen was the same as that measured previously to 7,000 in the gas apparatus at liquid air temperature.<sup>11</sup> Measurements were made successfully with a single set-up to 30,000 at 30° and 75°. Zero creep or other seasoning effects were now almost imperceptibly small, doubtless because of the mechanical softness, and the greater magnitude of the change of resistance.

The experimental results are given in Table I. At 30° and 10,000 the present value of  $\Delta R/R_0$  is  $-0.1262$  against  $-0.1266$  found formerly. Second degree extrapolation at 30° from 5,000 and 10,000 now gives  $\Delta R/R_0 = -0.3726$  against  $-0.2959$  observed. The discrepancy is in the opposite direction than for the four previous metals. The second degree relation is thus not nearly as good an approximation as for the other metals in which the absolute magnitude of the pressure effect is less. If  $\log(-\Delta R/R_0)$  is plotted against pressure a curve is obtained which does not depart greatly from linearity, being gently convex toward the pressure axis. If now a second degree curve is passed through the 15,000 and the 30,000 points of this logarithmic curve, extrapolation indicates a minimum in resistance at 82,000 kg/cm<sup>2</sup>. The only conclusion is that if there is a minimum it is probably well beyond present experimental possibilities.

*Lithium.* The material was from Kahlbaum. It was extruded into a wire about 0.030 inches in diameter, and connections made with spring clips. Successful runs were made to 30,000 at 30° and 75° with a single set-up. The maximum difference between points with increasing and decreasing pressure was at 75°, where it was 1 per cent of the maximum pressure effect. The effect was not a zero creep, but rather a permanent alteration of resistance after application of the maximum pressure; this might well be due to mechanical distortion in this relatively soft metal.

The numerical results are given in Table II. The resistance of

TABLE II  
RESISTANCE OF LITHIUM

Pressure kg/cm <sup>2</sup>	Resistance		Pressure kg/cm <sup>2</sup>	Resistance	
	$R/R(0, 30^\circ)$ 30°	$R/R(0, 75^\circ)$ 75°		$R/R(0, 30^\circ)$ 30°	$R/R(0, 75^\circ)$ 75°
2,500	1.0175	1.0172	17,500	1.1318	1.1339
5,000	1.0354	1.0351	20,000	1.1524	1.1553
7,500	1.0539	1.0537	22,500	1.1735	1.1770
10,000	1.0727	1.0730	25,000	1.1949	1.1992
12,500	1.0920	1.0928	27,500	1.2169	1.2221
15,000	1.1117	1.1131	30,000	1.2394	1.2453

lithium has been previously measured to 12,000. The resistance increases under pressure and at an accelerated rate, the curve of resistance against pressure being convex toward the pressure axis. Although this is the direction of curvature for all metals with positive pressure coefficient, with the exception of antimony, it was of particular interest to find whether the upward curvature would continue, in view of a suggestion which has been made theoretically that the resistance might pass through a maximum at high enough pressures. Inspection of the Table shows that the upward curvature does indeed continue up to 30,000. The first differences are nearly linear in the pressure, which means a second degree relation between resistance and pressure.

The increment of resistance found formerly at 10,000 at 30° was 7.57 per cent against 7.27 found now. The direction of the difference would indicate higher purity in the present sample. Another indication in the same direction is that the temperature coefficient at atmospheric pressure found now is very materially higher than the previous value. However, I do not give the figure for this coefficient,

since the possibility of chemical action was not ruled out by making a return check reading at  $30^\circ$ .

*Sodium.* The material was from the same source as that used in my previous measurements of volume to 20,000.<sup>1</sup> It was extruded into wire about 1.3 mm in diameter, and connections made with spring clips of fine wire, as with lithium. A run was made at  $30^\circ$  to 30,000 and back to 12,000, when one of the leads open circuited. Since the primary question with regard to this substance, namely whether there was a minimum in the resistance, was answered by these measurements, I did not attempt to complete the measurements by setting up the apparatus again, but as already explained, preferred to use the time in measurements on other substances.

The results are shown in Table III, in which are shown also my

TABLE III  
RESISTANCE OF SODIUM

$R/R(0, 30^\circ)$			$R/R(0, 30^\circ)$		
Pressure	Present	Former	Pressure	Present	Former
kg/cm <sup>2</sup>	Values	Values	kg/cm <sup>2</sup>	Values	Values
2,500	.8529	.8515	17,500	.5049	.5021
5,000	.7537	.7480	20,000	.4813	
7,500	.6762	.6731	22,500	.4619	
10,000	.6171	.6141	25,000	.4456	
12,500	.5708	.5671	27,500	.4324	
15,000	.5341	.5308	30,000	.4223	

previous results for comparison.<sup>12</sup> The agreement, particularly at the high pressures, is satisfactory. The previous measurements reached a maximum of 18,000; from these measurements I extrapolated the curve of first differences to a probable minimum at 28,000. This pressure was exceeded in the present measurements, but the minimum does not occur below 30,000, which simply means that the curve of first differences is not as nearly linear above 18,000 as I drew it. In fact the curvature is so great that extrapolation now appears more hazardous than before; it seems to me now that the most probable location of the minimum is in the neighborhood of 40,000. But it must be admitted that if I had only the data for sodium without those of the other alkali metals also, I would now have much less assurance of even the existence of a minimum than I had when I had only the measurements up to 18,000.

*Potassium.* The material was from Kahlbaum; it was extruded to bare wire and mounted for the resistance measurements in the same

way as lithium and sodium. At  $30^\circ$  a successful run was made to 30,000 and back. At  $75^\circ$ , the highest reading was made at 25,000; on trying for the maximum pressure the lower reinforcing ring on the outside of the pressure cylinder ruptured, the only time a similar accident has occurred in all this work. I did not attempt to complete the measurements with another set-up. At  $30^\circ$  there was some divergence between the runs with increasing and decreasing pressure, doubtless because of mechanical distortion of this very soft metal. The readings with decreasing pressure at  $30^\circ$  were taken as most probably accurate. Neither was any attempt made to get very accurate values at the lowest pressures, where the change of resistance is so large that any extrapolation to zero would have been inaccurate. Instead, the low pressure values were so chosen as to agree with my former values up to 5,000. At  $75^\circ$  the values under 5,000 were inaccurate. Also because of the impossibility of checking the zero at  $75^\circ$  there may have been an error at the lower pressure due to chemical action such that all the tabulated resistances may be too high with regard to those at  $30^\circ$  by a constant factor.

The most interesting question presented for the measurements on potassium is whether the minimum of resistance expected on the basis of my previous measurements<sup>12</sup> to 18,000 actually occurs. My former extrapolated value for the pressure of the expected minimum was 23,500. Table IV shows at once that the minimum does occur.

TABLE IV  
RESISTANCE OF POTASSIUM

Pressure kg/cm <sup>2</sup>	$R/R(0, 30^\circ)$		Pressure kg/cm <sup>2</sup>	$R/R(0, 30^\circ)$	
	$30^\circ$	$75^\circ$		$30^\circ$	$75^\circ$
0	1.000		22,000	.1760	
2,500	.664		23,000	.1740	.216
5,000	.491	.615	24,000	.1726	
7,500	.378	.467	25,000	.1719	.216
10,000	.303	.372	26,000	.1721	
12,500	.253	.310	27,000	.1729	
15,000	.219	.269	28,000	.1740	
17,500	.197	.242	29,000	.1756	
20,000	.1821	.224	30,000	.1778	
21,000	.1788				

In the lower part of the Table are shown the results in the neighborhood of the minimum at  $30^\circ$  to one more significant figure than in the rest of the Table. The measurements were accurate enough to give

the *relative resistance* to four figures; the absolute resistances, however, are not accurate to four significant figures. At  $30^\circ$  the minimum appears to be at 25,400, about 2,000 higher than the previously extrapolated value. The discrepancy is in the same direction as found already for sodium, but by not so large a factor, as would be expected because the extrapolation is not over so wide a range. At  $75^\circ$ , the minimum is perceptibly lower, at about 24,000. This shift in pressure of the minimum with temperature means that in the neighborhood of this pressure there is a notable increase in temperature coefficient of resistance; for pressures up to this point the variation of temperature coefficient with pressure is not large, as is also the case with most other metals.

*Rubidium.* The material was from the same lot as that used in my previous measurements.<sup>12</sup> This metal is so soft that the difficulties of using it in the form of wire seemed prohibitive; it was therefore enclosed in a glass envelope. The envelope was in the form of a *U*, the upper ends of the legs of the *U*, in which were sealed the platinum leads, being about 3 mm inside diameter, and the lower part of the legs, containing the part subjected to measurement, about 2 mm in diameter and 2 cm long. The proportions were made short and thick in order to minimize the restraining effect of the glass. If the *U* is long and slender the differential compression of the glass and rubidium demands so much relative motion that there is much distortion, and the column may even be ruptured. The *U* was filled in vacuum. The filling apparatus was provided with four successive chambers, and the rubidium was driven from one chamber to the next by distillation at the lowest feasible temperature, each chamber being sealed off in turn as it was emptied of its charge. In this way the impurity of oxide, which dissolves in the metal, can be removed. Previous work had shown no appreciable metallic impurities. The walls of the *U* were made as thin as convenient in the hope that they would completely rupture under pressure, leaving the metallic rubidium unconstrained. This was not accomplished with complete success however; the glass ruptured, but it ruptured into slender longitudinal slivers, so that the distance between the potential terminals was still set by the glass and its compressibility, instead of by the rubidium. Since the compressibility of rubidium is greater than that of glass, the distance between the potential terminals is greater under pressure than it would be if the metal were free, and, to compensate, the cross section must be less. Both effects work together in making the resistance under pressure too high.

Two attempts were made with this metal. The second yielded measurements at  $30^\circ$  up to 30,000, back to 22,000, up to 26,200, and back to 20,700, before there was open circuit. I made no further attempt to complete the measurements at  $75^\circ$ . The results on the initial increase of pressure are summarized in Table V. These values

TABLE V  
RESISTANCE OF RUBIDIUM

Relative Resistance at $30^\circ$			Relative Resistance at $30^\circ$		
Pressure kg/cm <sup>2</sup>	Present Values	Former Values	Pressure kg/cm <sup>2</sup>	Present Values	Former Values
0	1.000	1.000	17,500	.358	.310
2,500	.615	.656	20,000	.376	.314
5,000	.471	.504	22,500	.404	
7,500	.407	.416	25,000	.447	
10,000	.371	.364	27,500	.504	
12,500	.354	.333	30,000	.576	
15,000	.350	.316			

are not particularly good for the absolute resistance, because of unknown effects connected with the constraint exerted by the glass and the inevitable distortion of a metal as soft as this, which resulted in permanent alterations of resistance after application of pressure, so that successive excursions did not give coincident readings.

Rubidium is already known from previous work to have a minimum in its resistance. The principal interest of these measurements over an extended range did not therefore lie in establishing the existence of the minimum, but rather in determining whether there is a polymorphic transition between 20,000 and 30,000. One might be expected because of analogy with caesium, which I had already found to have such a transition. Very careful exploration was made for a discontinuity in the resistance of rubidium, which would indicate a transition, taking readings much closer together than usual, but no effect was found. I do not believe that a discontinuity in resistance of more than 0.0003 of the initial resistance would have escaped detection. We shall presently see that the discontinuity in resistance at the transition of caesium is 0.04, so that it is highly improbable that rubidium has a transition in this range. This negative result was confirmed by measurements of the volume in the other apparatus.

The pressure of the minimum of resistance given in the table above is 15,000, against the value 17,000 found before. Because the previous measurements were made with bare wire, there is no doubt that

they are to be preferred. The former values of  $\Delta R/R_0$  are also given in the table for comparison. The present values lie too high, as was to be expected because of the character of the constraint. It was a surprise that the divergence was not greater; it was not nearly as great as would be demanded by the difference of compressibility, assuming the glass to be perfectly effective in exerting constraint.

Besides the question of minimum and transition point, it was also of interest to find whether the upward curvature in resistance continues over this new pressure range. A plot of first differences against pressure shows that they get larger numerically at an accelerated rate at the upper end of the pressure range, so that the upward curvature increases. However, the deviation from linearity between first differences and pressure is only slight, so that this conclusion has to be taken with reserve because of the unknown effect of constraint by the glass.

TABLE VI

## RESISTANCE OF CAESIUM

Pressure kg/cm <sup>2</sup>	$R/R(0, 30^\circ)$		Pressure kg/cm <sup>2</sup>	$R/R(0, 30^\circ)$	
	30°	75°		30°	75°
0	1.000		20,000	1.917	2.369
2,500	.807		22,070	2.203	
				2.439	
5,000	.812	1.046	22,420		2.932
7,500	.884	1.117			3.056
10,000	1.005	1.260	22,500	2.492	3.068
12,500	1.169	1.450	25,000	2.836	3.491
15,000	1.376	1.685	27,500	3.239	3.972
17,500	1.624	1.984	30,000		4.509

*Caesium.* The material was freshly obtained from Mackay, provided sealed in glass tubes, not under oil, but clean metal. A number of attempts were made before a successful pressure run was made. Like rubidium, it was impossible to work with the bare metal, but it had to be sealed in glass. The final method was the same as that finally adopted for rubidium in the light of experience with caesium. With the final filling runs were made at both 30° and 75° up to about 29,000, and then again at 30°. Caesium has a minimum in resistance at low pressures; the feature to be particularly studied in these measurements was the effect of passing through the transition near 22,000 which had already been established with the 50,000 apparatus. The

readings were surprisingly regular, and were almost exactly reproducible with increasing and decreasing pressure. This was not to be expected in the light of the results with rubidium, and in view of the

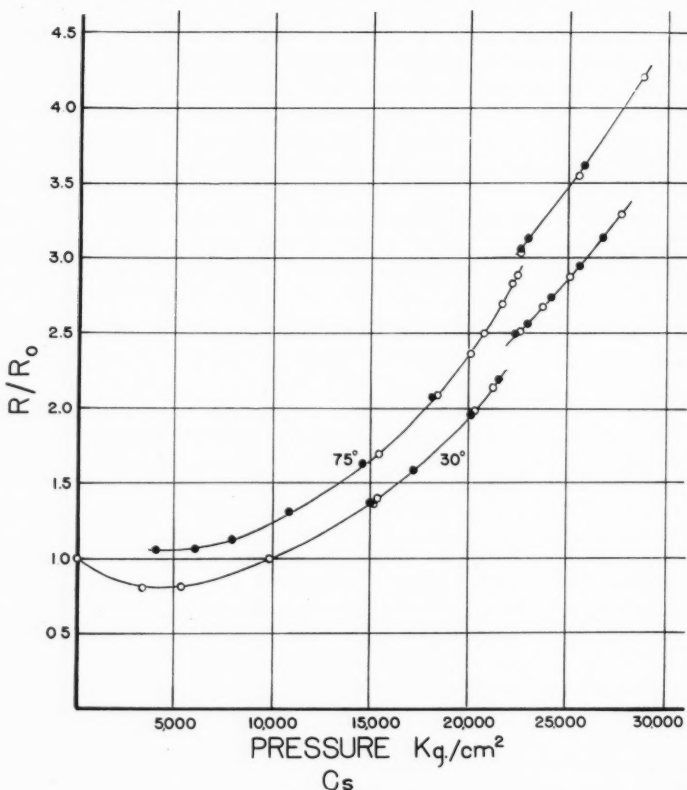


FIGURE 5. The relative resistance of caesium as a function of pressure at  $30^\circ$  and  $75^\circ$ . Open circles, increasing pressure; filled circles, decreasing pressure.

constraint exerted by the glass. One arm of the glass *U* did not even crack under pressure, and the other received only a single longitudinal crack for its entire length. The results are shown in Table VI and also in Figure 5. There is an *upward* jump in resistance at the transi-



tion point, in spite of the decrease of volume. There is only one other known example of this sort of behavior, Bismuth II to Bismuth III, in which the resistance change at a transition point runs contrary to

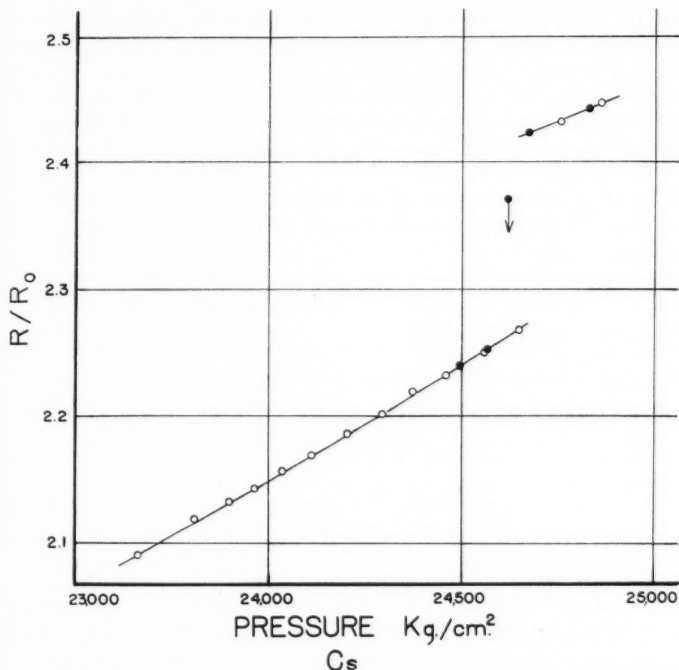


FIGURE 6. Relative resistance of caesium on a much enlarged scale in the neighborhood of the phase change. Open circles, increasing pressure; filled circles, decreasing pressure. The arrow on one point indicates that equilibrium was not reached, but resistance was decreasing in the direction indicated.

the direction of volume change. Furthermore, the resistance of the new modification also increases under pressure, and with upward curvature. There is, however, a very marked drop in the magnitude of the positive pressure coefficient on passing the transition point.

The second run at 30° was especially devoted to getting the transition point as accurately as possible and to finding how sharp the

transition is. Readings were made at intervals of only 100 kg/cm<sup>2</sup> up and down through the transition. The apparatus has to be handled carefully to give such small pressure steps; in making the manipulations advantage was taken of the fact that the resistance of caesium is much more sensitive to pressure changes under these conditions than is the manganin gauge. In Figure 6 are plotted the points obtained in this way. The sharpness of the transition was a great surprise, there being no appreciable transgression of the transition point in either direction, a very unusual effect, particularly with such a small amount of material. The transition was shut between two pressures from above and below differing by only 23 kg/cm<sup>2</sup>. This would seem to suggest that the mechanism of transition is something unusual. At 75° I did not make such elaborate attempts to determine the transition accurately, but within the corresponding greater uncertainty no lag phenomena were found; the transition was actually enclosed between limits differing by 400 kg/cm<sup>2</sup>. The transition pressure increases somewhat with rising temperature, being 22,070 at 30° and 22,420 at 75°. The discontinuity of resistance at the transition is a strong temperature function, being 10.6 per cent at 30° and only 4.2 per cent at 75°. In fact the two curves suggest that at still higher temperatures the direction of discontinuity might reverse. The direction of change of resistance at the transition may therefore be more or less accidental.

The temperature coefficient of resistance of II above the transition is very nearly the same as that of I below the transition. It may be at once concluded from the table that the mean coefficient 0°–100°, assuming a linear relation between resistance and temperature, of I at 15,000 and 20,000 is 0.00553 and 0.00581 respectively, whereas that of II at 22,500 and 27,500 is 0.00570 and 0.00556 respectively. The coefficient of I appears to decrease markedly with rising pressure at the lower pressures, being 0.00709 at 5,000. All these values are somewhat uncertain because of the constraining effect of the glass.

*Calcium.* The material was extruded wire obtained from the General Electric Co. some 15 years ago. It has been kept since in a bottle with cork stopper impregnated with paraffin. Protection from oxidation had not been perfect, perhaps one third of the diameter of the wire being oxidized away. The oxide layer was rubbed off with emery paper, leaving a shiny metallic wire, flexible enough to permit a single sharp bend with care. Connections were made with spring clips in the conventional way. Two runs were successfully made to 30,000 at 30° and 75° with a single set-up and without accident. There

was some seasoning effect at 30°, the final zero being displaced by 2.8 per cent of the maximum pressure effect, or about 1.25 per cent on the total resistance. At 75° there was no appreciable difference between increasing and decreasing measurements. This also indicates freedom from chemical action, so that a satisfactory value of the temperature coefficient should be obtainable from the difference of zero readings, in spite of the fact that a return check reading at 30° was not made. It would appear that whatever the nature of the seasoning effect, it had been completed by the first application of 30,000. For this reason the measurements at 30° used in the final calculations were those obtained with decreasing pressure. The points were always regular, the maximum departure of any single point from a smooth curve being at 75°, 0.07 per cent of the maximum pressure effect.

TABLE VII  
RESISTANCE OF CALCIUM AND STRONTIUM

Pressure kg/cm <sup>2</sup>	Calcium $R/R(0, 30^\circ)$		Strontium $R/R(0, 30^\circ)$	
	30°	75°	30°	75°
0	1.0000	1.1688	1.0000	1.0974
2,500	1.0237	1.1922	1.1141	1.2140
5,000	1.0490	1.2187	1.2448	1.3451
7,500	1.0764	1.2485	1.3922	1.4908
10,000	1.1069	1.2816	1.5562	1.6510
12,500	1.1407	1.3178	1.7364	1.8258
15,000	1.1772	1.3571	1.9333	2.0153
17,500	1.2164	1.3998	2.1467	2.2195
20,000	1.2582	1.4460	2.3767	2.4377
22,500	1.3025	1.4959	2.6273	2.6703
25,000	1.3491	1.5485	2.8905	2.9187
27,500	1.3983	1.6033	3.1695	3.1805
30,000	1.4500	1.6603	3.4665	3.4585

The smoothed results are given in Table VII. The curves are smooth, with no particular feature. First differences increase nearly linearly with pressure over the entire range at both temperatures, so that the resistance can be represented as a function of pressure very nearly by an expression in the second degree. The temperature coefficient of resistance depends markedly on pressure, being 0.00417, 0.00376, and 0.00357 at 0, 15,000 and 30,000 respectively.

The effect of pressure on the resistance of calcium has been previously measured.<sup>14</sup> The former values for the relative increase of

resistance at 30° at 5,000 and 10,000 were 0.0548 and 0.1199 respectively against the present values 0.0490 and 0.1069. The new values are thus considerably lower. This means greater purity in the present sample. Greater purity is also vouched for by the higher value of the temperature coefficient at atmospheric pressure, 0.00417 against the former value 0.00333. The new value is higher than the highest value reported in the literature,<sup>15</sup> 0.0038, whereas the former value was distinctly low. The much greater mechanical softness of the new sample compared with the old is also an indication in the same direction.

*Strontium.* The material was obtained from Eimer and Amend a number of years ago, and has been kept since under oil in a glass stoppered bottle. There has been appreciable surface chemical action. The surface was scraped to the pure metal, and the specimen formed into wire about 0.030 inches diameter by hot extrusion. Connections were made with spring clips as usual.

Three unsuccessful attempts, vitiated by leak or trouble with the insulating plug, were made before the fourth and successful attempt. Two runs were then made with a single set-up to 30,000 at 30° and 75°. Open circuit developed on the final reading at 75°, so that the check readings could not be made for temperature coefficient. There was no consistent difference between the readings with increasing and decreasing pressure, which, however, were not as smooth as usual. The maximum deviation of any reading from a smooth curve was at 30° at 27,000, the point lying high by 1 per cent of the total resistance at that point. Few of the other departures from smoothness were as much as one fifth of this.

The smoothed results for proportional resistance are given in Table VII. The resistance increases under pressure by a larger factor than for any other substance yet examined, the increase at 30,000 being by a factor of approximately 3.5. The curvature continues upward over the entire range, first differences against pressure rising linearly, so that a second degree equation in the pressure very approximately represents the results. The rate of increase is somewhat less at the higher temperature.

This specimen of strontium is probably of comparatively low purity, as shown by the low temperature coefficient, 0.00240, against my former value 0.00383. Unfortunately my former very pure strontium was exhausted. It appears from the table that the temperature coefficient reverses sign at the very upper end of the pressure range. This is highly unusual, and may well be an effect of the impurities.

At any rate, these data should not be used for a temperature coefficient; it has been my experience that the pressure coefficient is much less sensitive to impurity. There is nevertheless an anomaly in the pressure coefficient; my former value for the relative resistance at  $30^{\circ}$  and 10,000 was 1.606, against 1.556 now found. The lower value is usually associated with higher purity; this cannot be the case here.

*Barium.* My old supply of barium was exhausted; this was new stock, obtained from Mackay. The purity was not as high as that of the former, as suggested by the low value of the temperature coefficient of resistance, which was of the order of 0.004 against 0.0065 before. The metal was formed into wire of diameter 0.0030 inch by hot extrusion, and connections were made with spring clips as usual. Instrumental difficulties accumulated capriciously in an unusual degree in working with this material, and six different set-ups were made in all. The difficulties were almost always failure of insulation of the leads. There was also appreciable chemical action during a run, so that the readings with decreasing pressure did not follow those with increasing pressure, but the resistances with decreasing pressure lay high. A mean of the increasing and decreasing readings was taken as the best, but there were irregularities which would particularly affect the location of the minimum resistance, which previous measurements<sup>16</sup> had shown to be possessed by this substance. According to my custom, the measurements were made on this substance, roughly plotted to ensure against any large discrepancy, and then put away for exact calculation at a later time. After the measurements of resistance had been thus completed, the compression was measured in the 50,000 apparatus, and a small but perfectly definite transition discovered. This transition is of the ice type, running from 17,500 kg/cm<sup>2</sup> at  $0^{\circ}$  C to 15,300 at  $200^{\circ}$ , with an average volume change of 0.00155 cm<sup>3</sup>/gm, or 0.56 per cent on the volume. On returning to the measurements of resistance it then appeared that there was a small break in the resistance at  $75^{\circ}$  on decreasing pressure, at a little less than 15,000. The resistance readings at  $30^{\circ}$  and with increasing pressure at  $75^{\circ}$  were at too wide intervals and were too irregular to show any discontinuity. The apparatus was accordingly set up again for repetition of the resistance measurements. Again there were difficulties with the insulation at  $30^{\circ}$ , but a new set-up for  $75^{\circ}$  gave perfectly good results. Regular readings at short intervals were made in the range from 14,000 to 21,000, and breaks in the resistance found. The break occurred at 19,200 with increasing pressure and 14,900

with decreasing. The break with decreasing pressure thus occurs at practically the same place as had been found before. The mean pressure of the breaks, 17,050, is to be compared with 16,700, the equilibrium pressure at  $75^\circ$  found with the volume apparatus. The agreement is as close as could be expected in view of the width of the region of indifference.

The discontinuity in resistance is a drop with increasing pressure, thus being in the normal direction, that is, following the change of volume. The break is somewhat greater with decreasing pressure than with increasing, which means that the positive pressure coefficient of resistance of the high pressure modification is slightly greater than that of the low pressure modification. The discontinuity with decreasing pressure was very nearly the same on repetition as had been found at first. This suggests that the volume change during the transition repeated itself, with no geometrical distortion. This again suggests that the high pressure modification as well as the low pressure modification has some simple cubic structure. The average break in resistance was 0.35 per cent of the initial resistance.

The transition phenomena of barium thus are quite unlike the transition phenomena of caesium in the sluggishness and width of indifference of the transition. It is probable therefore that the mechanism of the transition, that is, nucleus formation and the geometry of the change of position from one lattice to another, is distinctly different in the two cases. However, it is to be remembered that the effective temperature in barium is very much lower than that of caesium because barium is so much further from its melting point. Because of the error due to the width of the region of indifference I did not take the trouble to try for accurate measurements of the transition at  $30^\circ$ .

Caesium and barium are alike in some aspects of the behavior of resistance in passing through the transition. Usually resistance is very sensitive to changes of volume, but here the resistance is little affected, the transition occurring with small discontinuity in resistance and with very little change in the direction of the curve.

The large scale irregularities were great enough to mask the effect of the transition, so that in smoothing the results one could smooth right over the transition, ignoring its existence. The resistances smoothed in this way are given in Table VIII. In broad outline the behavior is the same as for all other metals: upward curvature increasing with pressure. Compared with previous results, the variation with pressure is not quite so great as before, and the minima are

located at somewhat higher pressures. The former values for relative resistance at 30° at 5,000 and 10,000 were 0.968 and 0.965 against 0.971 and 0.970 found now. The minima were formerly found to occur at 9,100 and 9,600 at 30° and 75° respectively, against 7,750 and 9,500 found now. The former results are doubtless to be preferred because of the greater purity of the former material.

TABLE VIII

## RESISTANCE OF BARIUM

Pressure kg/cm <sup>2</sup>	R/R(0, 30°)		Pressure kg/cm <sup>2</sup>	R/R(0, 30°)	
	30°	75°		30°	75°
0	1.000	1.156	17,500	.995	1.123
2,500	.982	1.130	20,000	1.008	1.140
5,000	.971	1.114	22,500	1.025	1.161
7,500	.967	1.107	25,000	1.044	1.184
10,000	.970	1.106	27,500	1.066	1.211
12,500	.976	1.108	30,000	1.092	1.241
15,000	.984	1.113			

*Mercury.* The particular object of the run was to get measurements on the resistance of solid mercury over a more extended range than the 12,000 kg/cm<sup>2</sup> investigated hitherto,<sup>17</sup> and also to obtain a value for the melting pressure at a higher temperature. The mercury was ordinary distilled laboratory stock; which previous experience had shown to be amply pure enough since it gives sharp freezing points. It was mounted in a very thin glass *U*, with four platinum leads sealed in. The procedure was to first make measurements on the liquid phase at 30° with increasing pressure until the freezing pressure was reached. On completion of freezing, measurements were then made on the solid up to 30,000, and then back to a pressure sufficiently above the freezing pressure so that there was no danger of melting. Pressure was then raised to above the freezing pressure at 75° as extrapolated from previous measurements, temperature raised to 75°, readings made with increasing pressure up to 28,000, and then back in steps of 1,000 until the melting point was reached. Fortunately the final setting was made almost exactly on the melting point, permitting an accurate evaluation of the melting pressure at 75°. It was possible to be sure of this because the increase of resistance indicating melting did not begin to manifest itself until after waiting nearly ten minutes at constant pressure, which is more than the time required under normal conditions for complete attainment of temper-

ature equilibrium. The reason that melting did not take place at once was that at first on reaching this pressure the temperature was slightly depressed as a result of the decompression, and only after waiting some time did temperature creep back to the melting point. Previous experience with other materials would indicate that the maximum temperature effect of decompression is only a small fraction of a degree under these conditions, so that the melting coordinates should be fairly exact. On further release of pressure at  $75^\circ$  below the melting pressure the circuit opened, as was expected, because of escape of liquid mercury from the ruptured capillary, rupture doubtless having taken place on the first freezing at  $30^\circ$ .

All the experimental points, on both solid and liquid phases, were very regular and with no hysteresis, the departure from a smooth curve being hardly perceptible in any case. At  $30^\circ$ , the lowest reading on the liquid was at about 4,000 kg/cm<sup>2</sup>. The zero was calculated so as to make the change of resistance for the first 4,000 kg agree with my previous measurements.

TABLE IX  
RESISTANCE OF MERCURY

Pressure kg/cm <sup>2</sup>	Resistances Liquid	Pressure kg/cm <sup>2</sup>	Resistances Solid	
	$R/R_0$ $30^\circ$		$R/R(13,590, 30^\circ)$ $30^\circ$	$75^\circ$
0	1.0000	13,590	1.000	
4,000	.9076	15,000	.967	
6,000	.8635	17,500	.917	
8,000	.826	20,000	.871	
10,000	.792	22,500	.830	.987
12,000	.761	25,000	.793	.940
13,590	.738	27,500	.760	.897
		30,000	.730	.857

The numerical results are give in Table IX. The resistances of the solid are given in terms of the resistance at the freezing point at  $30^\circ$ . This freezing pressure, 13,500 kg/cm<sup>2</sup>, was obtained by an extrapolation from 12,000 of my previous measurements. The values for the liquid are relative to the resistance of the liquid at atmospheric pressure at  $30^\circ$ , the zero having been determined, as already explained, so as to make the change of resistance at 4,000 agree with the former value. In all cases, the resistances tabulated are the measured resistances. The specific resistance differs from this by a factor depending



on the change of dimensions. For the liquid phase, the change of dimensions is that of the glass capillary. The compressibility of the glass was not known. If an average value 0.0000024 (cubic compressibility per kg/cm<sup>2</sup>) is assumed, it will be found, for example, that the specific resistance of the liquid at 10,000 is 0.7858 of its initial value, against 0.7863 in my previous measurements. The agreement is as close as could be expected in view of the unknown difference between the compressibility of the glass capillaries in the two experiments. The measured resistances of the solid, on the other hand, are probably not at all affected by the glass, which was thin and had ruptured. Absence of constraint by the glass was also indicated by the complete absence of any pressure hysteresis. The measurements on the solid are therefore strictly comparable with the measurements on other solid substances in this paper, namely, they are measurements of the resistance between terminals attached to the specimen. The correction factor to convert to specific resistance is the linear compressibility of the solid; this is not known for solid mercury under these conditions.

On freezing at 30° the resistance dropped by a factor of 2.99. If it can be assumed that freezing took place without rupturing the glass capillary, some information can be extracted from the value of this ratio. This is somewhat smaller than the rough average found in my previous work. The crystal structure of mercury is tetragonal, and the ratio of the resistances along the two axes at atmospheric pressure is 0.756,<sup>18</sup> the resistance along the tetragonal axis being, abnormally, the lower. It is not unlikely that the solid measured above was mostly a single crystal, since freezing took place very slowly (it could be followed by following the change of resistance). The low value of the ratio, values obtained under ordinary conditions being in the neighborhood of 4, would therefore mean that the predominant orientation was with the tetragonal axis perpendicular to the axis of the specimen. The pressure coefficient measured above may, therefore, be the pressure coefficient for this predominant direction.

The pressure coefficient of resistance of the solid is high, being in the neighborhood of  $-0.00002$  at the freezing point at 30°. This may be compared with  $-0.000014$  for lead. At the freezing point at 30° the rate of change with pressure of the resistance in ohms of a specimen with fixed dimensions is somewhat greater in the solid than the liquid phase. This means that the *coefficient* of the solid is more than three times as great as that of the liquid at the freezing point.

The temperature coefficient of the solid may be computed from the

table. It is somewhat greater than  $1/\tau$ , as would be expected for a soft metal with a low melting point, and decreases somewhat with rising pressure, being 0.00467 at 22,500 kg and 0.00426 at 30,000.

The freezing pressure at  $75^\circ$  was 22,570 kg/cm<sup>2</sup>. Previous measurements up to  $20^\circ$  had shown the melting curve to be very nearly linear in pressure, the first differences increasing slightly. If it be assumed that the first difference increases linearly, being 1,980 kg/cm<sup>2</sup> per  $10^\circ$  at  $20^\circ$  and 2,010 at  $80^\circ$ , it will be found that the extrapolated melting pressure at  $75^\circ$  is 22,595 against 22,570 measured above. *Linear* extrapolation from  $-30^\circ$  and  $+20^\circ$  gives 22,446 kg/cm<sup>2</sup> at  $75^\circ$ . The presumption is that the manganin pressure gauge is not far off. The curvature of the melting curve of mercury is among the smallest, if not the smallest, of any measured.

*Zinc.* Measurements were made on two single crystal specimens, the identical specimens which I had previously used up to 7,000 at liquid air temperature.<sup>19</sup>

TABLE X  
RESISTANCE OF SINGLE CRYSTAL ZINC

Pressure kg/cm <sup>2</sup>	Axis $87^\circ$ to length $R/R(0, 30^\circ)$		Axis $17^\circ$ to length $R/R(0, 30^\circ)$	
	$30^\circ$	$75^\circ$	$30^\circ$	$75^\circ$
0	1.0000	1.1627	1.0000	1.1650
2,500	.9868	1.1488	.9758	1.1352
5,000	.9744	1.1355	.9525	1.1062
7,500	.9628	1.1228	.9300	1.0809
10,000	.9518	1.1107	.9081	1.0562
12,500	.9416	1.0991	.8882	1.0325
15,000	.9321	1.0880	.8686	1.0103
17,500	.9233	1.0776	.8500	.9890
20,000	.9150	1.0677	.8321	.9687
22,500	.9072	1.0582	.8153	.9495
25,000	.8998	1.0498	.7990	.9310
27,500	.8926	1.0420	.7835	.9129
30,000	.8855		.7687	.8959

(1) Axis inclined at  $87^\circ$  to the length. At  $30^\circ$  a successful run was made up to 30,000 and back; at  $75^\circ$  with the same set-up readings were obtained only with increasing pressure up to 25,000; at 30,000 a permanent ground developed on one of the leads. At  $30^\circ$  there was a permanent increase of resistance of unexplained origin between 25,000 and 30,000, amounting to 1.3 per cent of the initial resistance. The decreasing curve ran parallel to the increasing curve. The decreasing

curve at  $30^\circ$  and of course the increasing curve at  $75^\circ$  were used to give the final results. All points at both temperatures lay on smooth curves without perceptible deviation. There is no indication of a discontinuity, and therefore of a transition.

The results are given in Table X. The first differences are convex toward the pressure axis, the curvature of the line of first differences becoming greater at the high pressure end of the line. The data give no basis for an estimate of a hypothetical pressure at which there might be a minimum resistance. The temperature coefficient of resistance is nearly constant over the entire pressure range, increasing very slightly at the higher pressures.

Previous measurements on a specimen with axis oriented at  $90^\circ$  to the length give for the proportional change of resistance at  $30^\circ$  and 10,000 0.0467, against 0.0482 above.

(2) Axis inclined at  $17^\circ$  to the length. Successful runs were made with a single set-up at both  $30^\circ$  and  $75^\circ$  up to 30,000 and back. At  $75^\circ$ , two points lay off a smooth curve by 0.7 per cent of the maximum effect; otherwise there were no important deviations.

The results are given in Table X. Comparison with previous results is not as simple as for the other orientation, and I have not attempted it. The first differences drop very nearly linearly with pressure, but with slight convexity toward the pressure axis. Any possible minimum of resistance is too remote for profitable speculation, particularly since shearing measurements make it probable that there is a polymorphic transition below 50,000. Again the temperature coefficient is very nearly independent of pressure.

The pressure coefficient is higher in the  $17^\circ$  orientation than in the other by an amount considerably higher than the difference of specific resistance in the two directions, so that as a consequence the ratio of specific resistances at first approaches equality as pressure increases. In fact, the variation of pressure coefficient with direction is so great that at 30,000 the relative resistances along the axes have reversed, the ratio at  $17^\circ$  to that at  $87^\circ$  being 0.90 against an initial ratio of 1.035. This effect is very far above any possible experimental error; it is an interesting point for the theorist.

*Tin.* Measurements were made on two single crystal samples, the same as those previously measured to 7,000 at liquid air temperature.<sup>20</sup>

(1) Axis  $17^\circ$  with the length. Successful measurements were made at  $30^\circ$  and  $75^\circ$  up to 30,000 and back with a return check reading at  $30^\circ$ . The points lay very smoothly, with no hysteresis, and no suggestion of any discontinuity that might mean a transition. The maximum

deviation of any single point from a smooth curve was 0.2 per cent of the maximum pressure effect.

The results are given in Table XI. The relation between pressure and resistance is very nearly of the second degree in the pressure, there being a slight deviation in the direction of greater curvature at the lower pressures. Previous measurements on this sample gave for the average pressure coefficient of resistance 0—10,000 at  $-79^{\circ}$   $-9.79 \times 10^{-6}$ , against the value  $-9.51 \times 10^{-6}$  at  $30^{\circ}$  found now.

TABLE XI  
RESISTANCE OF SINGLE CRYSTAL TIN

Pressure kg/cm <sup>2</sup>	Axis $17^{\circ}$ to length $R/R(0, 30^{\circ})$		Axis $82^{\circ}$ to length $R/R(0, 30^{\circ})$	
	$30^{\circ}$	$75^{\circ}$	$30^{\circ}$	$75^{\circ}$
0	1.0000	1.1734	1.0000	1.1793
5,000	.9500	1.1139	.9538	1.1257
10,000	.9049	1.0598	.9125	1.0764
15,000	.8636	1.0111	.8754	1.0309
20,000	.8262	.9671	.8418	.9905
25,000	.7924	.9274	.8102	.9533
30,000	.7617	.8905	.7815	.9191

The temperature coefficient is again nearly independent of pressure.

(2) Axis oriented at  $82^{\circ}$  to the length. A first attempt with this sample gave results only to 25,000 at  $30^{\circ}$ , beyond which there was an open circuit. A second set-up gave two complete runs at  $30^{\circ}$  and  $75^{\circ}$  up to 30,000 and back. The values obtained with the second set-up were those finally used. The first set-up gave at its maximum pressure a value agreeing exactly with that of the second, with a maximum discrepancy at intermediate pressures of 0.5 per cent of the maximum pressure effect. The maximum deviation from a smooth curve of any single reading of the second set-up was 0.2 per cent of the maximum pressure effect.

The results are shown in Table XI. Again the relation between pressure and resistance is nearly of the second degree, but with a deviation in the direction of greater curvature at the lower pressures which is somewhat greater than with the other orientation. The temperature coefficient of resistance is also nearly independent of pressure, being 0.00442 at atmospheric pressure and 0.00434 at 30,000.

Unlike the results with zinc, the pressure coefficient of resistance in different directions is much more nearly equal than the specific resistances themselves in those directions, so that there is little change

with pressure of the ratio of resistance along the two axes. What little change there is is in the direction of increasing equality of resistance at high pressure.

*Antimony.* Measurements were made on two single crystals of different orientations, the identical specimens which had been previously measured to 7,000 at liquid air temperature.<sup>21</sup>

(1) Axis 87° with the length. Two set-ups, yielding only incomplete results because of leak and insulation trouble, were first made. The third set-up yielded a complete run at 30° to 30,000 and back, but at 75° readings could be made only to 15,000, beyond this the insulation going bad. There were indications of previous trouble with the insulation, the points at 30° not lying as regularly as usual. There were two bad points, lying off the curve by 1 per cent of the total resistance, but the other points lay smoothly, and the results should be essentially correct.

TABLE XII  
RESISTANCE OF SINGLE CRYSTAL ANTIMONY

Pressure kg/cm <sup>2</sup>	Axis 41° to length $R/R(0, 30^\circ)$		Axis 87° to length $R/R(0, 30^\circ)$	
	30°	75°	30°	75°
0	1.0000	1.1993	1.0000	1.1975
2,500	1.0246	1.2260	1.0140	1.2035
5,000	1.0547	1.2553	1.0263	1.2072
7,500	1.0894	1.2866	1.0372	1.2091
10,000	1.1264	1.3196	1.0456	1.2091
12,500	1.1633	1.3528	1.0512	1.2067
15,000	1.1978	1.3845	1.0529	1.2017
17,500	1.2289	1.4141	1.0496	1.1927
20,000	1.2557	1.4408	1.0421	
22,500	1.2781	1.4639	1.0288	
25,000	1.2959	1.4798	1.0104	
27,500	1.3085	1.4942	.9850	
30,000	1.3151	1.4996	.9533	

The relative resistances are given in Table XII. The resistance at first increases with pressure, then passes through a maximum, and then drops. Antimony is the only example with a maximum resistance and with curvature concave toward the pressure axis. Unless there is a polymorphic transition, there must of course be a reversal of curvature at still higher pressures, because if this curvature were to continue the resistance would presently become negative. It is,

however, highly probable that there is a polymorphic transition<sup>22</sup> below 50,000.

The effect of pressure on resistance is an unusually strong temperature function. The maximum resistance occurs at 14,500 kg/cm<sup>2</sup> at 30° and at 8,800 at 75°. The curvature at 75° is considerably greater than at 30°. This results in an abnormally great decrease of temperature coefficient with increasing pressure; the coefficient is 0.00487 at atmospheric pressure, 0.00334 at 10,000, and 0.00297 at 17,500.

(2) Axis inclined at 41° to the length. A single set-up was made with this sample, yielding at 30° a complete run to 30,000 and back, and at 75° only readings with increasing pressure up to 25,000, beyond which one of the insulating stems pinched off. The readings before the final accident were entirely regular, with barely perceptible deviation from a smooth curve.

The results are given in Table XII. The resistance initially increases with pressure with normal curvature, that is, increases at an accelerated rate, but presently in the neighborhood of 5,000 there is a point of inflection, and from here on the curve rises with concavity toward the pressure axis, and is evidently headed for a maximum like the other orientation, but at considerably higher pressure. The extrapolated pressure of the maximum is just beyond the experimental range, being 31,250 at 30° and 30,250 at 75°. The variation of maximum pressure with temperature is thus not as great as with the other orientation. The temperature coefficient again drops markedly with pressure, but not by quite as much as for the other orientation; the coefficient is 0.00491 initially, 0.00320 at 15,000, and 0.00263 at 30,000.

At atmospheric pressure the resistance of single crystal antimony is highly anomalous in that the resistance for flow across the cleavage plane is less than for flow in it. Comparison of the results above for the two orientations shows that at high pressures the difference reverses sign, so that antimony becomes normal in that at a pressure roughly in the neighborhood of 13,000 the ratio of resistance in the two directions becomes equal, and at pressures above 13,000 the ratio is normal, the discrepancy in resistance becoming accentuated at an accelerated rate as pressure increases.

*Bismuth.* Measurements have previously been made up to nearly 20,000.<sup>23</sup> Bismuth has two transitions beyond 23,000;<sup>24</sup> so that there was not much point in repeating these measurements in order merely to obtain a 3,000 kg increase of range, but there was very great interest in finding the behavior of the new modifications.

Measurements were made with a single set-up, on a single crystal sample with axis inclined at  $78^\circ$  to the length, the same sample as used in previous measurements to 7,000 at liquid air temperature. With this sample a successful run was made at  $30^\circ$  up to 29,000 and back, through the two transitions in both directions. At  $75^\circ$  readings

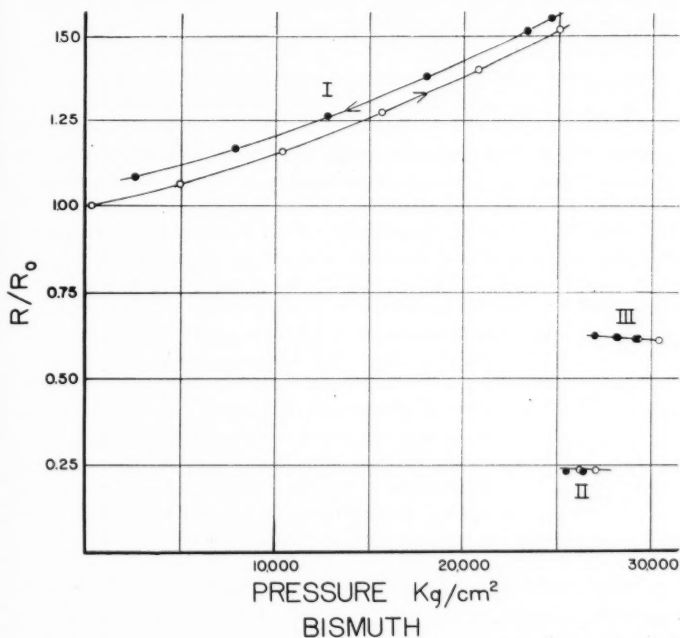


FIGURE 7. The relative resistance at  $30^\circ$  as a function of pressure of the three modifications of bismuth. Open circles, increasing pressure; filled circles, decreasing pressure.

were obtained only with increasing pressure up to 25,500, giving a reading on the third modification; beyond this there was open circuit due to pinching off of one of the stems.

The results are probably of sufficient interest to justify showing the actual experimental points, which are given in Figure 7 for  $30^\circ$ . The resistance increases with upward curvature on modification I in the way determined in previous experiments up to the transition to II.

Here there is an abrupt drop of resistance by a factor of something more than 6. The modification II is stable over only a narrow range of pressure. Measurements were obtained at two points in this range; the resistance of II drops slightly with rising pressure, as is normal. With further increase of pressure the transition to modification III is marked by an abrupt *rise* of resistance by a factor of more than 2.5. This rise of resistance is highly abnormal; it was the first example known in which the resistance on passing through a phase change (either liquid-vapor, liquid-solid, or solid-solid) goes contrary to the direction of the volume change. Since then one other example has been found, caesium, but this doubtless reverses in sign at higher temperatures. Measurements on III were made at several pressures up to 29,000 and back to the transition. Again the pressure coefficient is normal, the resistance decreasing with increasing pressure. Furthermore, the readings were reversible, the resistance under decreasing pressure retracing its course with increasing pressure. On passing the transition point from III to II, the resistance drops back by a large amount, but not to quite the former value. Failure of II to recover exactly its previous value is doubtless due to gross changes produced by the transition, probably a combination of changes of dimensions and changes in the orientations of the individual crystal grains. The latter effect would vanish if II were isotropic. There is, of course, no reason to anticipate that when the mono-crystal I transforms into II it transforms into another mono-crystal. The pressure coefficient of II with decreasing pressure is practically the same as with increasing, indicating no large change in effective orientation or else approximate isotropy of pressure coefficient of II. On further decrease of pressure, II transforms back into I; again there is the very large increase of resistance, and again the former value is not exactly regained. Release of pressure on I back to atmospheric now gives a curve with somewhat different slope from the initial slope, from which the certain conclusion can be drawn that I has not recovered its mono-crystal character. This was confirmed by subsequent examination of the specimen; it was covered with small-scale roughnesses, and the axis was no longer straight, but has several appreciable changes of direction. The over-all permanent change of dimensions was small. By comparing the initial and the final resistance it may be concluded that the transformation from the original mono-crystal to a completely haphazard aggregate is more than two thirds complete.

The run at  $75^{\circ}$  was similar as far as it went to that at  $30^{\circ}$ . Comparison between the two runs at  $30^{\circ}$  and  $75^{\circ}$  must not be pushed too far



in computing temperature coefficients etc. because of probable geometrical differences in the specimen at the two temperatures.

No extravagant attempt was made to get accurate values of the pressure of transition by taking very small pressure steps, as had been done for caesium. The size of the steps is sufficiently indicated in the figure. There was no observed over-shooting of either transition in either direction; the pressure steps were of such a size that any possible over-shooting could not possibly have been more than 1,000 kg/cm<sup>2</sup>. The transition pressures given here are the mean with increasing and decreasing pressure of the means of the extreme pressures on both sides of the transitions. The size of the pressure steps was such that the maximum error in the transition pressure should be of the order of 150 kg, assuming no over-shooting at all; the error would be somewhat larger if there was actually unobserved over-shooting within the allowable limits. At 75° the transition pressure could not be enclosed within such narrow limits, because the reverse readings were not made, except that the transition II-III should be fairly accurate because the slowness of the transition indicated that by accident the reversible transition point had been very nearly reached.

TABLE XIII

## RESISTANCE OF BISMUTH

Pressure kg/cm <sup>2</sup>	$R/R(0, 30^\circ)$	Pressure kg/cm <sup>2</sup>	$R/R(0, 30^\circ)$
	I	22,500	1.4513
0	1.0000	24,700	1.5141
2,500	1.0295		II
5,000	1.0648		
7,500	1.1060	24,700	.2389
10,000	1.1523	26,600	.2355
12,500	1.2036		III
15,000	1.2592		
17,500	1.3193	26,600	.6166
20,000	1.3833	30,000	.6041

The relative resistances at 30° are given in Table XIII. Only the increasing points for phase I are used here, so that this part of the Table refers to the orientation with axis 78° to the length. The resistances of II and III are means with increasing and decreasing pressure, and refer to some unknown average orientation, if these phrases are not isotropic. At 75° the relative values of resistance have less significance, because they refer to an unknown initial orientation in phase I. Hence I give for 75° merely some of the data connected

with the transition. The accuracy of the original measurements is great enough to justify giving certain data more accurately than they can be taken from Table XIII. These values now follow in Table XIV. The pressure coefficients of II and III given in this table are in terms of the resistances of these phases at their respective transition points taken as unity.

TABLE XIV  
DETAILS OF RESISTANCE OF BISMUTH AT TRANSITIONS

30°		75°	
$\left(\frac{R_I}{R_{II}}\right)_{24,700}$	= 6.339	$\left(\frac{R_I}{R_{II}}\right)_{23,500}$	= 5.92
$\left(\frac{R_{III}}{R_{II}}\right)_{26,600}$	= 2.618	$\left(\frac{R_{III}}{R_{II}}\right)_{25,500}$	= 2.32
Mean pressure coef. II, -0.06741		Mean pressure coef. II, -0.06776	
Mean pressure coef. III, -0.06597			

Previous Values of Transition Pressures

I-II	25,100	22,800
II-III	27,600	26,000

The former values of the transition pressures are given in the table for comparison. The discrepancy is never greater than the maximum of 1,000 set above. Measurement of pressure in the former apparatus was less sensitive than in this, so that, except for the uncertainty in the extrapolation of the manganin gauge, the new values should be preferred. Probably further work on this subject would be well worth while in connection with a more certain establishment of the pressure scale in this region. If it should prove that the transition is really much sharper than the utmost limit, 1,000 kg, allowed by the above, the transition pressure of bismuth at 30° might serve as a convenient calibration point in this region, because of the very large discontinuity in the resistance.

The temperature coefficient of II at a mean pressure in its range calculates to be 0.0047, but as already explained, this is uncertain because of the possibility of change of geometrical configuration.

*Tellurium.* Runs were made on two single crystal specimens of different orientations, the identical samples which had been previously measured up to 7,000 at liquid air temperature.<sup>25</sup>

(1) Axis oriented at 23.5° to the length. One successful run up to

30,000 was made with this at 30°. An attempt at 75° was terminated by leak. A second set-up resulted in similar failure at 75°. I did not pursue the matter further, so that for this orientation there are measurements only at 30°. The experimental points lay very regularly, with no perceptible hysteresis or deviation from a smooth curve to the number of significant figures given.

The results are shown in Table XV.

TABLE XV  
RESISTANCE OF SINGLE CRYSTAL TELLURIUM

Pressure kg/cm <sup>2</sup>	23.5° Orientation	86° Orientation	
	30° C log $R/R_0$	30° C log $R/R_0$	75° C log $R/R_0(30^\circ)$
0	0.000	0.000	9.689
2,500	9.720	9.616	9.304
5,000	9.278	9.261	8.965
7,500	8.973	8.934	8.670
10,000	8.698	8.640	8.410
12,500	8.453	8.378	8.182
15,000	8.239	8.145	7.980
17,500	8.054	7.937	7.803
20,000	7.890	7.754	7.647
22,500	7.743	7.592	7.510
25,000	7.614	7.448	7.390
27,500	7.501	7.321	7.285
30,000	7.401	7.210	7.194

(2) Axis oriented at 86° with the length. Successful measurements were made with a single set-up to 30,000 and back at both 30° and 75°. All the points lay smoothly, with almost no perceptible hysteresis or deviation from a smooth curve.

The results are given in Table XV.

Compared with the previous results up to 20,000,<sup>1</sup> no striking new effect appears in the next 10,000 kg/cm<sup>2</sup>. First differences of log  $R$  continue to decrease less rapidly than linearly with increasing pressure. Any eventual minimum in resistance is probably not reached for considerably more than another 10,000 kg/cm<sup>2</sup>, and there is a polymorphic transition before this pressure.<sup>26</sup> The effect of pressure is noticeably less for the 23.5° than for the 86° orientation. The resistance is initially less for the 23.5° orientation, so that as pressure increases the ratio of the resistance in different directions approaches equality. The ratio does not reverse sign, however, as it does for zinc.

At atmospheric pressure the temperature coefficient of resistance of tellurium is negative, which is characteristic of non-metallic semiconductors. This negative value becomes rapidly less numerically (for the  $86^\circ$  orientation) and has almost become positive at 30,000. A short extrapolation, about which there should be little doubt because of the approximate linearity of the curve, indicates that the temperature coefficient will become positive not far from 33,000. Previous results to 20,000 suggested the same behavior for the other orientation also. In respect to the temperature coefficient tellurium therefore approaches the behavior of a true metal at high pressure.

#### SUMMARY

I shall not attempt any theoretical discussion of the significance of these results. It is to be remarked, however, that the theoretical physicist is rapidly finding how to make wave mechanical calculations of resistance as a function of pressure, so that speculation on the theoretical significance of the results and comparison of theory and experiment may safely be left to those more competent. A brief summary of the results will, however, probably be worth while.

The comparatively hard metals, copper, silver, gold, and iron behave about as one would expect up to 30,000 from extrapolation of the behavior to 12,000. The deviation from the extrapolated value is in such a direction that any minimum of resistance probably occurs at a higher pressure than that extrapolated from measurements up to 12,000. For the softer metals of the remainder of the paper extrapolation from values up to 12,000 only proves hardly profitable. In general, the broad features of resistance found over the lower pressure range are preserved. With one exception, the resistance of all metals when plotted against pressure shows upward curvature, whether the coefficient is positive or negative. If the metal has a positive coefficient, the curvature usually increases at higher pressures.

Among the alkali metals, the resistance of sodium was found not to pass through a minimum below 30,000, as had been expected from previous work to 18,000, but the minimum now appears to be beyond 40,000. The minimum expected for potassium is actually realized not far beyond the anticipated pressure. The minimum of rubidium formerly found is verified; the resistance continues to increase regularly over the entire range beyond the minimum, with no hint of a transition. The resistance of caesium takes a jump upward at the transition pressure, a highly unusual effect. In general the resistance of caesium is much less disturbed than might be expected by the

transition through a change of lattice. The transition is very sharp. Theoretically this perhaps might not have been anticipated, because analytically the conditions which determine the transition seem to involve a delicate balance between two tendencies, both of them strong.

The alkali earth metals, calcium and strontium, continue their smooth upward increase of resistance over the entire range. Barium, however, shows a transition, with a very small change of resistance, and very little interruption of the smooth upward increase. The transition of barium is very sluggish, totally unlike that of caesium. Barium is body centered cubic, calcium and strontium both face centered. Difference in the behavior is therefore not surprising. The series of alkali metals is body centered cubic under normal conditions; it is highly probable that the high pressure transition of caesium is from body centered to face centered. By analogy one would expect the transition of barium to be also to face centered. But the parallelism between the alkali metal and the alkali earth series is far from perfect. The situation is complicated by the small transitions of calcium and strontium known to occur beyond the range of the present work. Serious speculation should wait for detailed calculations.

The resistance of solid mercury is found to behave about as would be expected from a soft metal in its position in the periodic table. The melting curve can be extrapolated over nearly double its former range with unexpected accuracy; the curvature of the melting line is abnormally low.

Single crystal zinc at high pressures shows a reversal of relative resistance along the axes, the resistance along the axis becoming less than at right angles, behavior which at atmospheric pressure would be classed as abnormal. Apparently wave mechanics is hardly yet in a position to undertake detailed calculations of the resistance of crystals in different directions, particularly under pressure. Single crystal tin in two orientations decreases smoothly in resistance over the entire range, with practically no change in the ratio of resistance in different directions. Single crystal antimony is the only known example of a metal whose resistance passes through a maximum with increasing pressure. This maximum occurs at lower pressures the more nearly the axis is perpendicular to the length, and the pressure of the maximum is a strong temperature function. Single crystal tellurium decreases in resistance under a pressure of 30,000 kg/cm<sup>2</sup> by a factor of the order of 600. It appears that at a pressure only slightly beyond 30,000 the temperature coefficient of resistance will reverse sign, becoming positive like a metal.

The resistance of bismuth at the I-II transition takes a downward jump by a factor of about 6, but at the II-III transition the resistance jumps up by a factor of about 2.5 against the change of volume. The only other example of a change of resistance against the change of volume is caesium, for which, however, the jump in resistance is comparatively small. The pressure coefficients of modifications II and III of bismuth are normal (negative), in spite of the fact that bismuth I is abnormal (positive coefficient). The behavior of bismuth is to be contrasted with that of caesium and barium, where a modification with positive coefficient transforms to another modification with only slightly different positive coefficient.

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